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Development of an equation for potentiometric titration of polyelectrolytes using a periodic lattice model

A numerical analysis of interactions among ionizable groups

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A numerical method is presented for analyzing the potentiometric titration behavior of linear polyelectrolytes. A polyelectrolyte molecule is treated as a one-dimensional lattice containing a large number of lattice points, each of which has an identical ionizable group. In this method, the polyelectrolyte model lattice is divided into identical repeating unit cell systems with a finite number of ionizable groups to calculate the thermodynamic partition function of the system of polyelectrolyte solution. The electrostatic interaction between ionized groups adopted in the present study is given by the Debye-Hückel type screened Coulombic potential. The titration behavior as well as several thermodynamic quantities is derived by making a canonical ensemble summation of all states in a unit cell system under an appropriate periodic boundary condition. This method serves as a model of the two-step ionization often appearing in polyions with strong neighboring interactions such as homo- and copolymers of maleic acid. Several characteristics of the titration behavior of these polyelectrolytes are well reproduced by using a lattice model with pairwise intervals, including the effects of hydrogen bond formation and change in dielectric constant of the medium around an ionizable group. In addition, this method is valid for a more detailed analysis of the titration behavior of polyelectrolytes with various kinds of arrangements of charged groups.

1. Introduction

Various theoretical studies have been performed to explain the potentiometric titration behavior of polyelectrolyte solutions. A rodlike model with a smeared charge has widely been applied to the dissociation of weak polyacids such as poly(acrylic acid) and poly(glutamic acid) by numerical solutions of the Poisson-Boltzmann (PB) equation [1,2]. The radius of the polymer rod used to fit the experimental data, however, sometimes became a physically unreasonable value [3,4]. More clearly, this method was found to be inapplicable to polyelectrolytes having higher charge densities than ordinary vinylic polyacids. These polyelectrolytes with high charge density often exhibited a two-step dissociation behavior, which was not explained by the smeared charge model. The importance of neighboring interaction has been suggested for the interpretation of abnormality in the titration of copolymers of maleic acid and other acids [5,6]. In the recent decade, several discrete-site models including neighboring interactions have been developed to analyze the titration behavior of various polyelectrolyte solutions [7–11]. The numerical methods have been incorporated into the interpretation of experimental results of polyacid solutions by the computation of the partition functions on the basis of a matrix method

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[12,13]. Although these investigations have clarified several of the properties of various kinds of homo- and copolymer systems, many disagreements were pointed out between the experimental results and theoretical data. For example, the titration curves observed are usually asymmetric with respect to the point at half ionization, which cannot be predicted by the method of this model [13,14]. Furthermore, the role of hydrogen bond formation and the effect of the dielectric constant change (dielectric saturation effect), investigated as other determinants of the titration profiles, have remained ambiguous points [12,13,15]. Therefore, it is valuable to estimate the contribution of the potential energy and other factors to the dissociation of polyelectrolytes from a different point of view. The evaluation of elementary thermodynamic quantities is also important for understanding the titration process.

In this study, a simple method is developed for analyzing the potentiometric titration behavior of polyelectrolytes by means of a one-dimensional lattice gas model, including interaction expressed by the long-range Debye-Hückel (DH) type screened Coulombic potential between the ionized groups. The canonical ensemble summation is numerically executed within a limited unit cell system in contrast with various approximation technique [10]. A rigorous computation is carried out on the basis of the elementary statistical thermodynamics. In spite of the relatively small number of ionizable groups (from 12 to 20) in a unit cell, the results are accurate enough to simulate the actual titration experiments. This method can be applied to a system with the molecular configuration of a real polymer and more appropriate types of the interaction potential.

With two typical examples of the polymer configuration, the titration behaviors and several thermodynamic quantities are computed and analyzed at various ionic strengths. The characteristic features of the method become apparent from the solutions of these typical cases. Moreover, the effects of hydrogen bonds and the change in the dielectric constant of the medium are estimated based on a simplified but essential hypothesis. The numerical results obtained by using these presumptions characterize the recent experimental data on the homo- and copolymers of maleic acid [12,14]. On the basis of these investigations, the interpretation of the titration experiments and the limitation of the hypothesis are also discussed.

2. Theory

2.1. General expressions of the potentiometric titration

The apparent dissociation constant K_a is used to analyze the titration behavior of polyelectrolytes. Its negative logarithm, pK_a, is defined in relation to the pH and the degree of ionization, α, as

$$pK_a = \mathrm{pH} + \log[(1-\alpha)/\alpha] \tag{1}$$

The value of pK_a increases with α due to the electrostatic interaction between ionized groups on a polyelectrolyte chain. It can be expressed by the sum of two terms as

$$pK_a = pK_0 + 0.4343(\mathrm{d}g_{el}/\mathrm{d}\alpha)/kT \tag{2}$$

where pK_0 is the negative logarithm of the intrinsic dissociation constant independent of α, g_{el}, the electrostatic free energies of dissociation per single group, k, the Boltzmann constant, and T, the absolute temperature. Throughout this paper, thermodynamic quantities in lower-case letters denote the values per single ionizable group. The electrostatic term of pK_a, ΔpK, is given by

$$\Delta pK = pK_a - pK_0 = 0.4343(\mathrm{d}g_{el}/\mathrm{d}\alpha)/kT \tag{3}$$

Since the nature of the pK_0 value is not taken into consideration in this study, the plot of ΔpK against α is denoted as the titration curve.

2.2. Definition of the linear lattice model

A rigid rod with N ($\gg 1$) ionizable groups arrayed to form a linear lattice is considered as a simple model of a polyelectrolyte molecule, as shown in fig. 1. The polyelectrolyte molecule is assumed here to be a polyacid in a salt solution. The position of each group on the lattice is denoted as r_i. The variable p_i indicates the state of each group, i.e., ionized or unionized

$$p_i = \begin{cases} 1 & \text{if group } i \text{ is ionized} \\ 0 & \text{if group } i \text{ is un-ionized} \end{cases} \tag{4}$$

The set of p_i, $\{p_i\}$, determines the state of the model polyelectrolyte. The total number of the possible states on the lattice is 2^N, including energetically equivalent states. The number of ionized groups and the degree of ionization of the lattice at each state are denoted as n_p and α_p

$$n_p = \sum_{i=1}^{N} p_i \tag{5}$$

$$\alpha_p = n_p/N \tag{6}$$

The energy of each ionized state, E_p, is divided into two parts, the energy of ionization of the groups at a given pH, $E_{s,p}$, and the electrostatic interaction energy between ionized groups, $E_{el,p}$,

$$E_p = E_{s,p} + E_{el,p}. \tag{7}$$

In the above equation, $E_{s,p}$ is defined as

$$E_{s,p} = \mu_s n_p \tag{8}$$

$$\mu_s = 2.3026(pK_0 - pH)kT \tag{9}$$

and $E_{el,p}$ is represented as follows

$$E_{el,p} = \sum_{\langle ij \rangle} \epsilon_{ij} p_i p_j \tag{10}$$

where ϵ_{ij} is the interaction energy between the i-th and the j-th groups and the summation is carried out over all combinations for different groups i and j. The Debye-Hückel type screened Coulombic interaction is applied to the potential energy of the pairs of ionized groups as

$$\epsilon_{ij} = \left(q^2/4\pi\epsilon_0 DkT\right) \exp(-\kappa r_{ij})/r_{ij} \tag{11}$$

where r_{ij} is the distance between the i-th and the j-th groups, and κ is the Debye-Hückel screening parameter, defined as,

$$\kappa^2 = \left(2e^2/\epsilon_0 DkT\right)(N_{AV} I/1000) \tag{12}$$

where S.I. units are used. In eqs 11 and 12, q is the charge of the ionized group, ϵ_0, the permittivity of vacuum, D, the relative dielectric constant of the solvent, e, the elementary charge, N_{AV}, Avogadro's constant, and I, the ionic strength of the solution, including the supporting salt. The electrostatic interaction energy between the ionized groups on the polyion and salt ions is assumed to be included in pK_0.

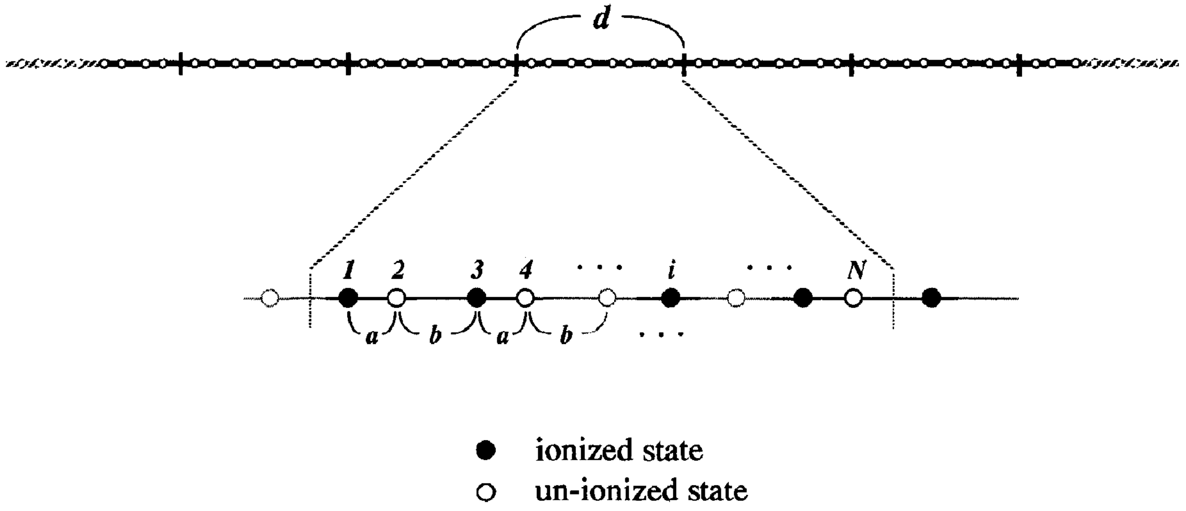

Fig. 1. Schematic representation of a model polyelectrolyte, which is divided into the unit cell of length d with pairwise configuration of N ionizable groups (lower lattice).

The canonical partition function of the system is defined as

$$Z_p = \sum_{\{p_i\}} \exp(-E_p/kT) \tag{13}$$

where the summation is taken over all possible states.

The degree of ionization α is defined as a statistical average as,

$$\alpha = \langle \alpha_p \rangle = \sum_{\{p_i\}} \alpha_p \exp(-E_p/kT)/Z_p \tag{14}$$

Other thermodynamic quantities treated in this paper are expressed as

$$u_{\mathrm{el}} = \sum_{\{p_i\}} E_{\mathrm{el},p} \exp(-E_p/kT)/Z_p/N \tag{15}$$

$$g_{\mathrm{el}} = -kT \ln Z_p/N \tag{16}$$

$$g_{\mathrm{el}} = u_{\mathrm{el}} - Ts_{\mathrm{el}} \tag{17}$$

where u_{el} and s_{el} are the contributions of the electrostatic interaction to the internal energy and to the entropy per single group, respectively. The Helmholtz and Gibbs free energies are not distinguished in this scheme. The relation of s_{el} to the total entropy of the system, s_{tot}, and the entropy of random mixing, s_{rand}, is described as

$$s_{\mathrm{el}} = s_{\mathrm{tot}} - s_{\mathrm{rand}} \tag{18}$$

where $s_{\mathrm{rand}} = -k[\alpha \ln \alpha + (1-\alpha)\ln(1-\alpha)]$.

The above formulations of the system are equivalent to that of the one-dimensional lattice gas system in the grand canonical ensemble, treated in the standard textbooks on phase transition theory [16,17]. If the formulations are replaced by those of the grand canonical ensemble, the energy of ionization per single group, μ_s, is equivalent to the chemical potential of the ionized group with reference to the un-ionized state in the absence of electrostatic interaction between the ionized groups. The practical procedures for the execution of canonical summation are described in section 3.

2.3. Hydrogen bond formation

Intramolecular hydrogen bond formation between adjacent carboxyl groups has been suggested in several experimental studies [18,19]. In these studies, the hydrogen bond with a single electronic charge between a COOH group and a COO$^-$ group was considered. In other simulation studies, the hydrogen bond is thought to be formed either between two COOH groups or between a COOH and a COO$^-$ group in several poly(carboxylic acids) [12,13,20]. Although a carboxyl group has a tendency to form a hydrogen bond with a solvent molecule, a more stable hydrogen bond is believed to be formed between two COOH or a COOH and a COO$^-$ group except for two charged groups if the molecular structure permits. The existence of a hydrogen bond was recently confirmed in homo- and copolymers of maleic acid (S. Kawaguchi et al., manuscript in preparation.). Quantitative measurements, however, have not yet been reported in sufficient amounts to discuss the type and the energy of the hydrogen bond.

In our model calculations, two types of simplified style of hydrogen bond formation are considered to investigate its fundamental effects on titration behavior (see fig. 2). The first type of hydrogen bond formation (type 1) is similar to that assumed in studies using a matrix method [12,13]. The possible hydrogen bond is introduced between two adjacent un-ionized groups and be-

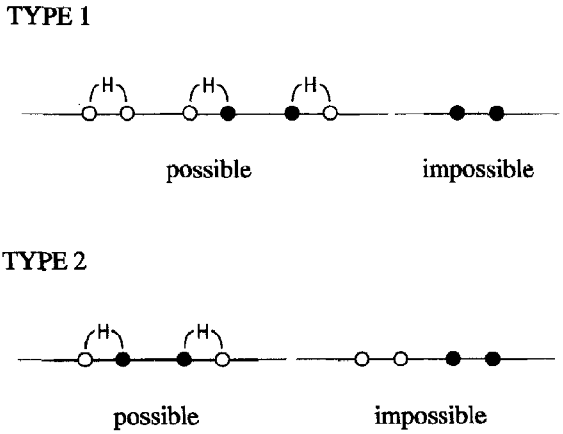

Fig. 2. Two types of hydrogen bond formation. Type 1 represents the possibility of the hydrogen bond between two un-ionized groups and that between an un-ionized and an ionized group. Type 2 represents the possibility of the bond between an un-ionized and an ionized group only.

tween a pair of ionized and un-ionized groups with the same bond energy. The second type (type 2) is the hypothesis of a hydrogen bond formed only between the pair of un-ionized and ionized groups. In both types, the hydrogen bond between the pair of ionized groups is inhibited.

The energy of the hydrogen bond corresponds to the difference in energies between the two above-mentioned groups and that between a group and a solvent molecule. Its value expressed by ϵ_h should be negative in the range of a few kT [21]. The canonical partition function of the system is given by the summation of all possible states with all acceptable hydrogen bond formations.

The formulation of the energy of each ionized state E_p, is represented instead of eq. 7 as

$$E_p = E_{s,p} + E_{el,p} + N_{h,p}\epsilon_h \tag{19}$$

where $N_{h,p}$ is the total number of the hydrogen bonds in a particular state of the system. The dissociation curves and other thermodynamic quantities are calculated as mentioned before. The statistical average of the number of hydrogen bonds per single ionizable group, n_h is defined as

$$n_h = \sum_{\{p_i\}} N_{h,p} \exp(-E_p/kT)/Z_p/N \tag{20}$$

By definition, the maximum value of n_h is 0.5.

As shown in fig. 2, pairwise bond formation is considered in the lattice unit cell. If the lattice spacing is changed alternately, the hydrogen bond is assumed to occur only for the pair with the shorter spacing. Several estimations are carried out with various values of the energy per single bond, ϵ_h, as a parameter. Through this effect, the titration curve is modified to exhibit a clearer jump in pK_a values at half neutralization.

2.4. Change in dielectric constant of the medium

The dielectric constant of water around a charged group is lowered by hydration known as the Sack effect [22]. Some works suggested that an effect is exerted by the decreasing dielectric constant near the ionized groups on the potentiometric titration behavior [6,12,15]. The value of the dielectric constant of water becomes a function of the distance from the central charged group [23,24]. The electrostatic interaction between charged groups is modified by this effect, resulting in a change in the pK_a profile with α, although the effect of the ionized group does not reach beyond a few ångstroms. A rigorous treatment of the effect on the titration profile, however, is not so easy because it depends on the steric arrangement of the charged groups. A simple way to estimate the effect of the decrease phenomenologically is to assume the dielectric constant of the medium (i.e., solvent water), D_p, to vary as a monotonic function of the degree of ionization in each state α_p. Namely, a linear function is adopted here,

$$D_p(\alpha_p) = D_0 - (D_0 - D_{\min})\alpha_p \tag{21}$$

where $D_{\min}$ is the minimum value of the dielectric constant at $\alpha_p = 1.0$, and D_0, the dielectric constant of water in bulk. Thus D_p can be substituted for D in eq. 11. Also, the Debye-Hückel screening parameter κ in eq. 12 is modified with the change in D_p.

The interpretation of the asymmetrical character of titration curves is expected on this presumption, although the effect of the change in the dielectric constant is probably overestimated owing to the simplification.

3. Computation

If the interaction between ionized groups is short-ranged, the partition function for large N-point lattice can be calculated with a matrix method [7–9]. Since the long-range interaction is also taken into consideration, the numerical computation of the partition function for a finite N-point lattice model is performed under a periodic boundary condition.

This is introduced such that a sufficient number of N-point unit cells in the identical state are connected to both sides of the central unit cell (see fig. 1). The length of a single unit cell is denoted as d. The sum of the interaction energies is made between an ionized group in the central cell and all other ionized groups both in the central cell and in the connected cells. This method provides a good approximation in evaluating the interaction energy in a long-chain molecule when the value of N is chosen to be not so high, instead of assuming a sufficiently large number for N. The formulations for the interaction energy, eqs 10 and 11, are modified, as

$$E_{\mathrm{el},p} = \sum_{\langle ij\rangle} \epsilon_{ij} p_i p_j + \epsilon_{\mathrm{u}} n_p \tag{22}$$

$$\epsilon_{ij} = \left(q^2/4\pi\epsilon_0 DkT\right) f(r_{ij}) \tag{23}$$

$$\begin{aligned} f(r_{ij}) = \sum_{m=0} \Big\{ & \exp\left[-\kappa(r_{ij}+md)\right]/(r_{ij}+md) \\ & + \exp\left[-\kappa((m+1)d - r_{ij})\right] \\ & /((m+1)d - r_{ij}) \Big\} \end{aligned} \tag{24}$$

$$\epsilon_{\mathrm{u}} = 2\left(q^2/4\pi\epsilon_0 DkT\right) \sum_{m=1} \left[\exp(-\kappa md)/md\right] \tag{25}$$

where m is the number of neighboring unit cells on both sides. In eq. 22, ϵ_{u} represents the contribution to the electrostatic energy between the equivalent ionized groups in neighboring unit cells in an identical state. Since this term shifts the titration curve upward, the length of the unit cell must be long enough to render the effect of ϵ_{u} negligibly small. When the potential energy of the pair of neighboring unit cells becomes negligibly small, the summation is truncated at an appropriate value of m, as discussed later.

Two configurations of the lattice are adopted as the model polyelectrolytes with the same average density of the ionizable groups in the present paper. Lattice A is an equidistance model lattice in which each distance between two adjacent groups is 2 Å ($a = b = 2$ Å, in fig. 1). In the case of alternating copolymers, the arrangement of ionized groups is not equidistant. Lattice B has a 1 : 3 distance ratio (e.g., $a = 1$ Å, $b = 3$ Å), corresponding to the latter case.

In these computations, rigorous accuracy in the calculated quantities is not achieved due to the limitation of the small group number N. The curves become not smooth but somewhat rippled as the value N is decreased. An effective method

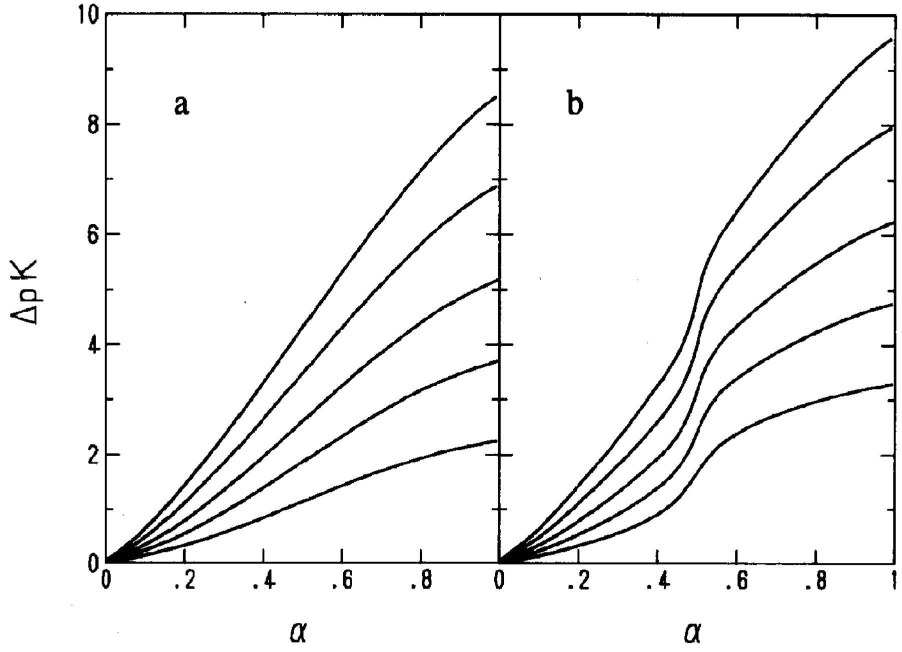

Fig. 3. Dependence of the titration curves on the ionic strength of the solution with (a) lattice A and (b) lattice B: $I = 0.01$, 0.03, 0.1, 0.3, and 1.0, respectively, from top to bottom.

to overcome this ambiguity is extrapolation by increasing the value N. Several computations are tried at different group numbers. Then, the thermodynamic quantities treated here are well approximated by setting $N \geqslant 12$, although the quantities related to their fluctuation are dependent on N. The calculated curves are sufficiently reliable without the extrapolation even if we adopt 12-point lattice, in which the total number of states is 4096. In the following computations, the results of the 20-point lattice are exhibited together with those of the 12-point lattice in the case of the hydrogen bond. The numerical constants used in the computation are $q = -e$ (single electronic charge), $T = 298.15$ K and $D = D_0 = 78.55$.

4. Results and discussion

4.1. Typical titration profiles

The titration curves under some typical conditions are presented in fig. 3. The equidistant lattice (lattice A) results in slightly sigmoidal titration curve as shown in fig. 3a. The change in ΔpK with α increases as the ionic strength decreases, due to the enhancement of the Debye-Hückel type Coulombic interaction. In fig. 3b, the results of a lattice polymer with 1 : 3 distance ratio (lattice B) exhibit a strongly sigmoidal feature at various ionic strengths as observed in maleic acid polymers [6,12,14]. By comparing fig. 3a with fig. 3b, the values of ΔpK in the low ionization range ($\alpha \leqslant 0.4$) are found to agree with each other at each ionic strength. This means that the ionized states which are energetically favorable are not affected by the lattice configuration at low degrees of ionization. In the case of lattice B, jumps of ΔpK values are found around $\alpha = 0.5$ and the width of the jumps increases as the ionic strength decreases. This biphasic dissociation process is due to the strong nearest-neighbor interaction of the pair of ionized groups with a shorter distance on the lattice. In all cases, a rotational symmetry of the curve around the half ionization point is observed. This symmetry appearing in the present

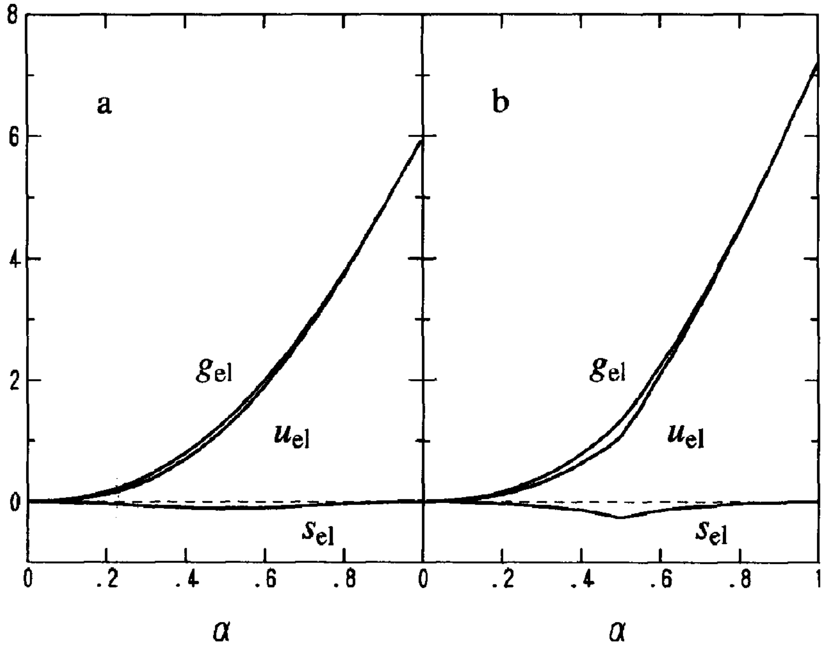

Fig. 4. The contributions of electrostatic interaction to the thermodynamic quantities. Solid lines denote g_{el}, u_{el} and s_{el}, respectively, from top to bottom, with (a) lattice A and (b) lattice B at $I = 0.1$. Each value is represented in kT units, and s_{el} divided by k. Broken lines: zero level.

calculation is interpreted by the general theories of phase transition [16,25].

One of the advantages of the method is the incorporation of long-range interactions between ionized groups. Although its contribution decreases rapidly with distance between the pair, the effect of the long-range interaction becomes significant as the ionic strength of the solution decreases. It is, however, sufficient to incorporate the interaction over a few neighboring unit cells on both sides of the central cell even at $I = 0.01$, according to the detailed analysis of the contribution. It is shown that the condition adopted for the truncation of the summation is sufficient to consider the long-range interactions.

4.2. Properties of the thermodynamic quantities

The values of various thermodynamic quantities are obtained by calculation, as mentioned before. In fig. 4, the contributions of the electrostatic interactions per single group to the Gibbs free energy, g_{el}, internal energy u_{el}, and entropy s_{el} are shown as a function of α for both lattice models at $I = 0.1$. It is noted that the contribution of the entropy term to the Gibbs free energy cannot be neglected. Therefore, the approximation, $\mathrm{d}g_{el}/\mathrm{d}\alpha = q\psi$ $(= \mathrm{d}u_{el}/\mathrm{d}\alpha)$, where ψ is an averaged electrostatic potential, is insufficient to calculate the titration curves of the polyelectrolytes with high charge density such as in this model [26].

The shifts of the entropy around $\alpha = 0.5$ suggest a tendency for alternating ionization due to the strong neighboring interaction. According to the investigation of the correlation function of the ionized groups, alternating ionization is indeed favorable even in an equidistance lattice. In the case of lattice B (fig. 4b), sharp curvature of u_{el} is observed at $\alpha = 0.5$, compared with the smooth curve of lattice A (fig. 4a). Although this contribution is partly compensated by s_{el} in g_{el}, the sharp curvature of the free energy forms a jump of pK_a at the half-ionization point. This indicates a stronger tendency of alternating ionization at $\alpha = 0.5$ in lattice B than in lattice A. Such an alternating tendency of the ionization state as well as width of the pK_a jump strongly depends on the lattice configuration of ionizable groups.

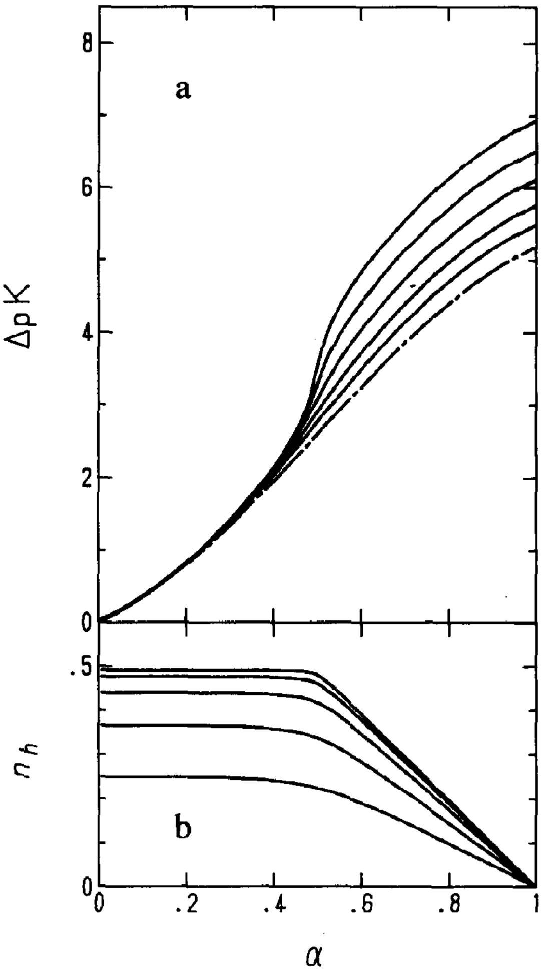

Fig. 5. Effects of hydrogen bond formation of type 1 on the titration curves (a) and the number of hydrogen bonds per single group (b) for lattice A at $I = 0.1$. $\epsilon_h = -4.0$, -3.0, -2.0, -1.0, and 0.0 in kT units, respectively, from top to bottom. Broken lines in (a) denote the cases of no hydrogen bond considered.

4.3. Hydrogen bond formation

The role of the hydrogen bond is probably significant in the titration process of the solution of several poly(carboxylic acids). It is thus valuable to estimate this effect.

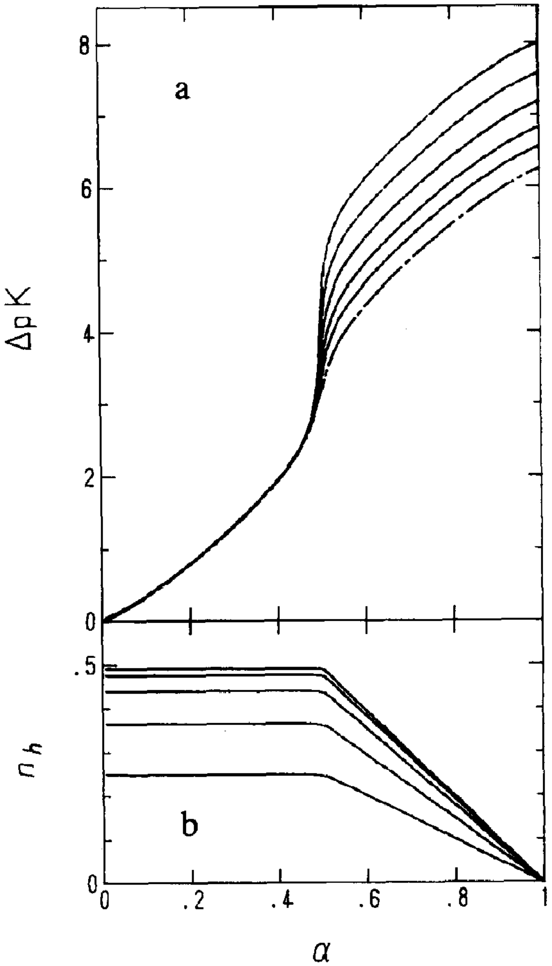

Fig. 6. Same as in fig. 5, for lattice B.

Figs 5 and 6 show the titration curves and the number of hydrogen bonds per single group, n_h, of lattice A and lattice B, respectively, according to the first hypothesis of the hydrogen bond (type 1) at $I = 0.1$. The increase in width of the jump around $\alpha = 0.5$, with decrease in hydrogen bond energy, ϵ_h is presented in figs 5a and 6a. The curves of n_h in figs 5b and 6b indicate a decreasing tendency of the number of bonds, which starts around $\alpha = 0.5$. These results indicate that the effects of the hydrogen bond still appear in the range of $\alpha > 0.5$ on the titration curves. This fact can be understood by considering the nature of the type of hydrogen bond formation. Several quantities contributed by the hydrogen bond are described at $\alpha = 0$ and at $\alpha = 1$, by the consideration of elementary statistical physics. At $\alpha = 0$, n_h, $dn_h/d\alpha$ and the additional term of the Gibbs free energy by the hydrogen bond, g_h, are presented as

$$\left.\begin{aligned} &n_h = 1/2\,\exp(-\epsilon_h/kT)/[1+\exp(-\epsilon_h/kT)]\\ &dn_h/d\alpha = 0\\ &g_h = -1/2\,kT\,\ln[1+\exp(-\epsilon_h/kT)] \end{aligned}\right\} \tag{26}$$

and, at $\alpha = 1$

$$\left.\begin{aligned} &n_h = 0\\ &dn_h/d\alpha = -\exp(-\epsilon_h/kT)\\ &/[1+\exp(-\epsilon_h/kT)]\\ &g_h = 0 \end{aligned}\right\} \tag{27}$$

The sharpness of the curvature of the n_h curves is dependent on the configuration of the lattice and the ionic strength. If there is a stronger alternating tendency of the ionized states, the curvature at the half neutralization point becomes sharper.

The additional term of ΔpK from hydrogen bond formation, $\Delta \mathrm{p}K_h$, at $\alpha = 1$ is expressed as

$$\Delta \mathrm{p}K_h = \log[1+\exp(-\epsilon_h/kT)] \tag{28}$$

Its magnitude is obviously dependent on the ϵ_h value only.

If the hydrogen bonding by a pair of un-ionized groups and a pair of ionized groups is inhibited (type 2), the titration behavior at $\alpha > 0.5$ is similar to that of type 1, as shown in figs. 7 and 8. In this case, the number of hydrogen bonds starts from 0 at $\alpha = 0$ and the ΔpK value shifts downward from the case of no hydrogen bond. This means that the ionization at low α is accelerated by hydrogen bond formation. Indeed, the first pK_a value of maleic acid monomer is very low. At $\alpha = 0$, n_h, $dn_h/d\alpha$ and g_h are represented as

$$\left.\begin{aligned} &n_h = 0\\ &dn_h/d\alpha = \exp(-\epsilon_h/kT)/[1+\exp(-\epsilon_h/kT)]\\ &g_h = 0 \end{aligned}\right\} \tag{29}$$

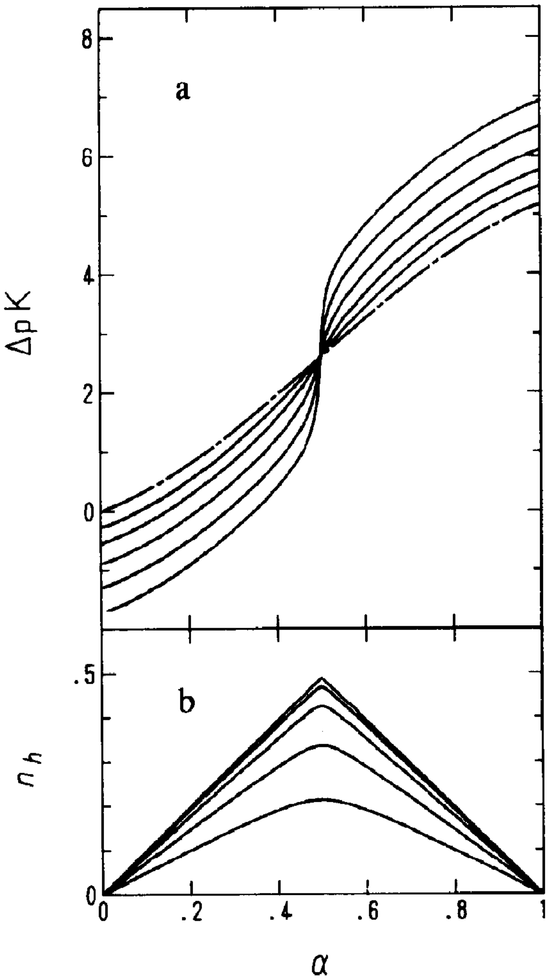

Fig. 7. Effects of hydrogen bond of type 2 on the titration curves and the number of hydrogen bonds per single group for lattice A at $I = 0.1$. Other details same as in fig. 5.

The whole width of the change in ΔpK_h from $\alpha = 0$ to $\alpha = 1$ is twice that in type 1 because the values of ΔpK_h at $\alpha = 0$ and at $\alpha = 1$ are described as follows,

$$\left.\begin{aligned} \Delta pK_h &= -\log[1+\exp(-\epsilon_h/kT)] \text{ at } \alpha = 0 \\ \Delta pK_h &= \log[1+\exp(-\epsilon_h/kT)] \text{ at } \alpha = 1 \end{aligned}\right\} \tag{30}$$

The sharpness of the curvature of n_h is dependent on the lattice configuration and the ionic strength of the solution in a manner similar to that of type 1.

Conclusively, it is noted that the formation of the hydrogen bond governs the width of the jump of titration curves around $\alpha = 0.5$. Therefore, more detailed information (type and energy of formation) on the hydrogen bond in the polyelectrolyte molecule is necessary to fit the experimental titration curve to the theoretical calculation.

4.4. Change in dielectric constant of the medium

One of the remaining difficulties is the interpretation of the asymmetrical feature of the titration

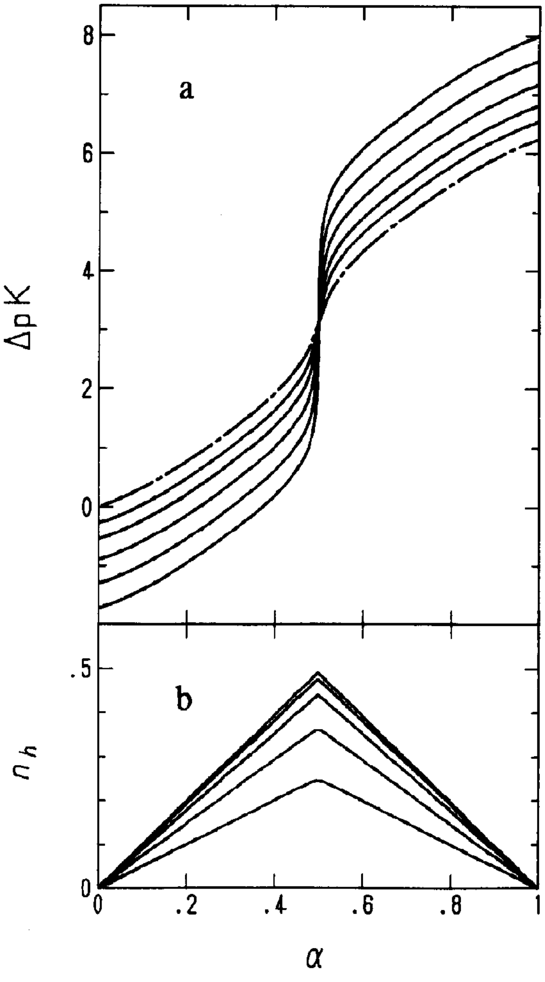

Fig. 8. Same as in fig. 7, for lattice B.

curves, observed in polyelectrolytes with a high density of the ionizable group. The titration curves often have steeper slopes in the region $\alpha > 0.5$ for polymers of maleic and fumaric acids [12]. In our scheme mentioned above, the symmetry of the titration curve persists under any condition. Since the normal lattice gas treatment also cannot avoid the symmetry, any parameter involved in the potential function should vary as a function of the degree of ionization in a unit cell of the model polyelectrolyte to introduce the asymmetrical feature. Then, considering the problem in the physical aspect, it is reasonable to introduce the change in dielectric constant of the solvent as a function of α. For convenience, a simple procedure of modification is applied such that the dielectric constant of the medium varies as a linear function of α in each state.

Fig. 9 shows the effects of the change in dielectric constant on the titration curves of 1 : 1 and 1 : 3 lattice, respectively, at various D_{min} values and $I = 0.1$. Asymmetrical curves, dependent on the minimum value of dielectric constant, are obtained in accordance with our expectation. Not only the steepness of the curve in $\alpha > 0.5$ but also the width of the pK_a jump at $\alpha = 0.5$ are strongly dependent on the value of D_{min}. This means that the interaction between the pair of ionized groups is affected by the states (i.e., ionized or un-ionized) of other neighboring groups. Through the simplified approximation, the effect of change in the dielectric constant is represented as a sufficient reason for the appearance of an asymmetric feature of the titration curves. Nevertheless, the value of D_{min} is not very reliable due to the oversimplification of the hypothesis. A more faithful approximation is required.

The steep slope of the titration curves at $\alpha > 0.5$ cannot be explained on the basis of the effect of counterion binding, as discussed later. A contribution by the conformational change of the polyelectrolyte chain to this asymmetry cannot be ruled out, since decreases in intrinsic viscosity are observed in this region [12,14]. Such contraction of the polymer chains possibly increases the electrostatic free energy of the ionization and makes the

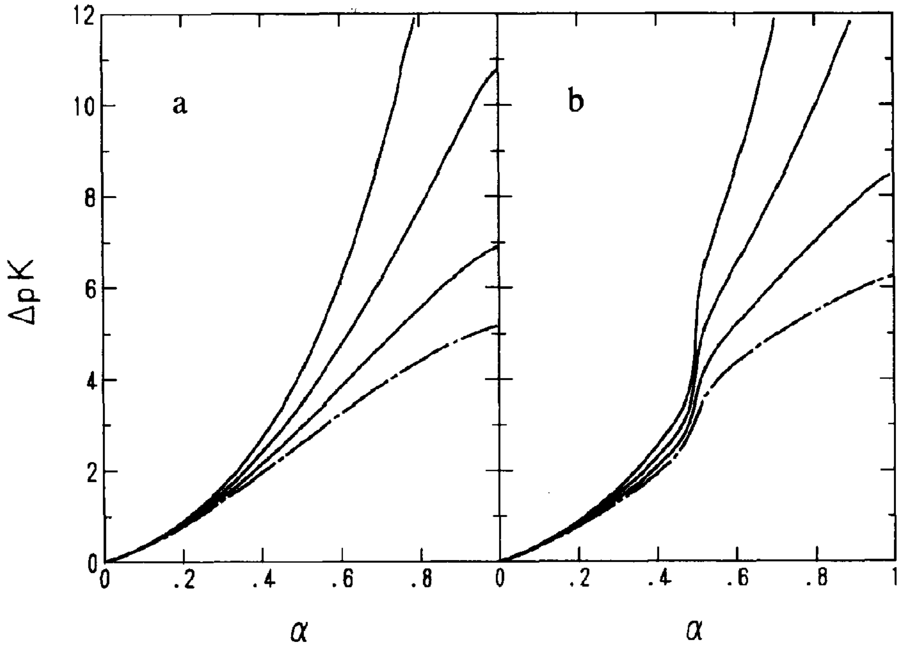

Fig. 9. Effects of change in the dielectric constant of the medium on the titration curve for (a) lattice A and (b) lattice B at $I = 0.1$. The dielectric constant of the medium is assumed to decrease linearly from $D_0 = 78.55$ to D_{min} as a function of α. $D_{\mathrm{min}} = 20.0$, 40.0, and 60.0, respectively, from top to bottom. Broken lines denote the unchanged cases.

titration curve steep. Estimation of this contribution should be considered as the remaining problem.

4.5. *Physical view of the ionization of polyelectrolytes*

From the microscopic point of view, the dissociation of an ionizable group gives rise to complicated processes. The ionization of a group on the polyelectrolyte molecule in aqueous solution leads to the reorientation of surrounding water molecules as well as the redistribution of small ions, which also leads to the hydration of water molecules, due to the electrostatic field. Re-formation of the hydrogen bond is also possible. Such hydration induces a decrease in the dielectric constant of the medium around the ionized group. The distribution of small ions near the ionized groups is dependent on the size and the valence of the ions. In addition, if the charge density on the polyion becomes higher than a critical value, territorial counterion binding, the so-called counterion condensation, should occur. Furthermore, the polyelectrolyte chain expands due to the electrostatic repulsive force and/or due to the effect of hydrogen bond formation unless the molecular backbone is sufficiently rigid. Finally, water molecules, small ions and the polyelectrolyte chain attain an equilibrium state, as a result of the interaction between each other [27,28]. Among these steps, the decrease in dielectric constant, counterion condensation, and chain expansion of the polyion produce the non-additive effects on the titration behavior.

It seems probable that the high charge density on a polyelectrolyte molecule leads to binding or condensation of counterions. Estimation of counterion binding has been studied with consideration of specific site binding and of the counterion condensation theory [8,29]. To include these effects in our method phenomenologically, the apparent ionic strength around the polyelectrolyte can be considered to be an increasing function of α as an adjustable parameter. Each approximation, however, is insufficient to explain the features of the titration curves of the polyelectrolytes, although all of these estimations can make the titration curves less steep as α increases, similar to the result of PB theory.

The effect of conformational change may be of importance for the flexible polyelectrolyte chain. To incorporate this effect, it is necessary to describe the free energy of the chain conformation and the electrostatic free energy with the expansion parameter. A careful investigation is required to resolve the problem, since the change in specific viscosity as well as the titration behavior should be interpreted by the incorporation.

To simulate the actual experimental curves, precise data on the polymer configuration and more reliable information on the hydrogen bond are necessary. In addition, the Debye-Hückel type potential function adopted here is not suitable for the interaction between the nearest neighboring ionized groups, because of the effect of hydrated water, ion type, etc. A further study is now in progress to consider these points.

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